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VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.ON CERTAIN SUBSTANCES OBTAINED FROM
TURMERIC.

BY C. LORING JACKSON AND A. E. MENKE.

Presented May 29, 1883.

OWING to the difficulty of preparing curcumin, and the very unmanageable nature of the products obtained from it and from turmerol, we have not made as much progress in the study of these substances as we had hoped. In fact, we should not publish our results at the present time, were it not that we cannot continue the work together at all, and neither of us will be able to return to it for at least a year; we have therefore decided to collect in the following papers all the results we have obtained up to this time, although many of them are very fragmentary, and others consist only in indications which may prove useful in future work.

IV. CURCUMIN.

Action of Acetic Anhydride on Curcumin.

Monacetcurcumin. $C_{14}H_{18}(C_2H_3O)O_4$. This substance is formed by the action of acetic anhydride and fused sodic acetate on curcumin, probably also by the action of acetylchloride. As has been stated in a previous paper,* it forms an uninviting brown resin, which we have not as yet succeeded in bringing into a crystalline condition; but nevertheless it can be obtained in a state of purity by the following method: Curcumin is heated on the water-bath with a slight excess of acetic anhydride and a little fused sodic acetate, for about sixteen hours, in a flask with a return-cooler; the dark brown viscous product is then dissolved in a little glacial acetic acid, and precipitated with water; after repeating the solution in acetic acid, and precipitation

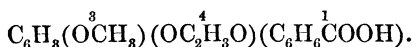
* These Proceedings, Vol. XVII. p. 123.

with water, the yellowish-brown precipitate is washed until free from acetic acid, and dried *in vacuo*.

0.1710 gr. of substance gave 0.4178 gr. of carbonic dioxide and 0.0922 gr. of water.

	Calculated for $C_{16}H_{16}O_5$.	Found.
Carbon	66.67	66.62
Hydrogen	5.55	5.99

Properties. A viscous brown mass without definite melting-point, although it shrinks together at 58° – 60° , but it does not become fully liquid below 100° . It is soluble in alcohol and glacial acetic acid, essentially insoluble in ligroine and carbonic disulphide, slightly soluble in ether and in benzol; but its solubility in the latter is greater than that of curcumin. It dissolves in strong sulphuric acid with a blood-red color like that produced by curcumin. Aqueous sodic hydrate dissolves it, forming a red solution, which becomes decomposed, with the formation of ill-defined black products, when allowed to stand exposed to the air; a mixture of alcohol and sodic carbonate was reddened instantly by the substance, showing that the acetyl group had replaced the hydrogen of the phenol hydroxyl, as was to be expected; that is, its formula would be



As has been stated already,* the substance gave unsatisfactory results when submitted to oxidation with potassic permanganate.

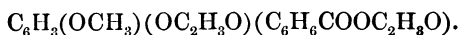
Diacetylcurcumin. $C_{14}H_{12}(C_2H_3O)_2O_4$. On one occasion the process described above yielded a yellow crystalline product instead of the brown viscous monacetylcurcumin. The coming of the vacation interrupted our work before we had succeeded in determining the conditions on which the formation of this substance depends, the few experiments which we had time to try giving invariably monacetylcurcumin; we must therefore, for the present, confine ourselves to describing the properties and analysis of the substance. After the removal of the acetic anhydride and sodic acetate by treatment with water, it was purified by washing with alcohol and crystallization from glacial acetic acid, dried at 100° , and analyzed.

0.2230 gr. of substance gave 0.5348 gr. of carbonic dioxide and 0.1090 gr. of water.

	Calculated for $C_{18}H_{18}O_6$.	Found.
Carbon	65.45	65.39
Hydrogen	5.45	5.43

* These Proceedings, Vol. XVII. p. 123.

Properties. It crystallizes from glacial acetic acid in rosettes of a vivid yellow color without the orange shade of curcumin, which are made up of very characteristic rhombic plates; melting-point, 154° . It is more soluble in glacial acetic acid than in any other solvent, especially when the acid is hot; less soluble in alcohol than curcumin; slightly soluble in ether and benzol; essentially insoluble in ligroine and carbonic disulphide. Strong sulphuric acid dissolves it, becoming blood-red in transmitted light, green like rosanilin in reflected light; the red color is somewhat more purple than that produced by curcumin. Sodid hydrate in aqueous solution acts upon it very slowly, and not rapidly, even if dissolved in dilute alcohol; the red solution thus obtained gives with hydrochloric acid a viscous brown mass with a low melting-point, which seems to be impure monacetcurcumin. Sodid carbonate and alcohol give an orange solution looking like that of potassic dichromate. According to the formula given by us to curcumin in our first paper, this substance should be a mixed anhydride of curcumin and acetic acid, with the other acetyl group attached to the phenol oxygen, as in the monacet-compound, — a constitution which would be expressed by the following formula: —



That the carboxyl group is affected by the introduction of the second acetyl is shown by the fact that alkaline reagents act upon it only after some time, and then evidently decompose it; whereas the monacet-compound is attacked by them instantly, and the action consists only in the formation of a salt: but, on the other hand, the substance is more stable than acid anhydrides are usually, as is shown by this very action with alkalies, and by the fact that it can be boiled with water for many hours without undergoing any change in melting-point, or the formation of any soluble acid.

Action of Phosphoric Oxychloride on Curcumin.

Of all the reactions of curcumin, which we have observed, this is by far the most striking, and we have decided therefore to describe it at some length, although we have not succeeded in determining the nature of the substance formed. If a few drops of phosphoric oxychloride are added to some curcumin suspended in ligroine, its orange-yellow color is converted instantly into a rich reddish purple, which in reflected light appears bronze-green with a metallic lustre, between the colors of rosanilin and Hofmann's violet. To prepare the substance in quantity, the curcumin was rubbed in a mortar with phosphoric

oxychloride diluted with ligroine and afterward washed repeatedly with ligroine; the dark purple viscous mass thus obtained was dried in a desiccator over sulphuric acid, lime, and paraffine. This treatment, the best which we could devise, was usually far from effectual, as in every case but one the substance contained phosphorus, and was invariably converted during drying into a black mass having very different properties from the purple viscous substance at first obtained. The analysis of the substance free from phosphorus gave results less than one per cent higher than those required by curcumin, and this was confirmed by the analysis of one of the preparations containing phosphorus, after the phosphorus present had been calculated as phosphoric acid, and subtracted from the weight of the substance.

The properties of the purple product are quite as striking as its formation from curcumin; for the addition of water converts it again into curcumin, and the change from purple to orange-yellow is instantaneous. That curcumin was formed in this case was shown by the melting-point, 178° . Alcohol also changes the color instantly from purple to yellow; but the product is much more soluble in alcohol than curcumin, and is possibly its ethylether. Ether acts in the same way, leaving, on evaporation, a viscous red mass; in ligroine and benzol it is essentially insoluble. By standing even in desiccator it is gradually decomposed — more rapidly at 100° — into a black mass, which is unaffected by water, but soluble in alcohol, or sodic hydrate forming dark solutions. Owing to the uninviting properties of this decomposition-product it was not studied further.

It is highly probable that the blood-red color imparted to strong sulphuric acid by curcumin is due to this substance, as curcumin is deposited when this solution is diluted. As to the nature of the purple substance, our analyses show nothing; but its easy conversion into curcumin by the addition of water indicates that it is an anhydride, and we are inclined to believe that the carboxyl of the curcumin alone is involved in the reaction, because we obtained a similar but somewhat redder color when monacetylcurcumin was treated with phosphoric oxychloride.

In our first paper on curcumin we assigned to it the formula



Our work since then has been directed toward the determination of the structure of the side-chain $\text{C}_6\text{H}_5\text{COOH}$, and, although we have

not succeeded in proving anything about it definitely, we may be allowed to state that our results can be explained by the assumptions that the carboxyl is attached to the carbon atom next but one to the benzol ring, and that in the remainder of the side-chain some of the carbon atoms are united to form a ring.

TURMEROL.

In our first paper on this subject we mentioned that, although turmerol is converted into terephthalic acid by treatment with an excess of a hot solution of potassic permanganate, the same reagent produces, when cold and not in excess, one or more apparently new acids. In the following paper we describe our study of the product of this reaction, a complex mixture of acids, from which we have succeeded in isolating two new acids, — one having the formula $C_{11}H_{14}O_2$, which we propose to call turmeric acid, the other either $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$, to which we would give the name apoturmeric acid.

In order to obtain this product, a little turmerol was allowed to stand at ordinary temperatures with a moderately strong solution of potassic permanganate until the latter was reduced. The operation was carried on in large beakers, and the yield seemed to be better when not more than 500 c.c. of permanganate solution were used in each oxidation, than when larger quantities were employed; with this amount the action came to an end in about three days. After the liquid had become colorless, the oxide of manganese and unaltered oil were removed by filtration, and again treated with permanganate solution; this treatment being repeated until the permanganate ceased to act, when it was found that the oxide of manganese was essentially free from organic matter, and therefore that the entire product was contained in the aqueous filtrate. The mixed filtrates from a number of operations were then concentrated on the water-bath, acidified with sulphuric acid, extracted several times with ether, and the extract, a black tarry liquid, distilled with steam, when a yellow oil (A) passed over with some difficulty; this was mostly turmeric acid. The residue in the flask (B) contained a tarry substance and apoturmeric acid, which not infrequently separated in white crystals as the solution cooled.

Upon distilling with steam the solution left after extraction with ether, it yielded a strongly acid distillate containing a little of the yellow oily acid, from which it was freed in great part by extracting it five times with ether. It was then boiled with baric carbonate to convert it into a barium salt, which crystallized, after it had evapo-

rated spontaneously nearly to dryness; the crystals, freed from mother-liquor by pressure between filter-paper, were nearly pure baric acetate, as shown by the following analysis:—

1.1745 gr. of the air-dried salt lost 0.0661 gr. when dried at 100°.

	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2\text{H}_2\text{O}$.	Found.
Water	6.59	5.63

1.1038 gr. of the dried salt gave 0.9974 gr. of baric sulphate.

	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$.	Found.
Barium	53.73	53.13

As, however, a solution of the silver salt blackened much more easily than argentic acetate should, and crystallized at first in balls made up of radiating needles, although after one or two recrystallizations attended by blackening it gave the flattened needles characteristic of argentic acetate, we suspected that there might be some other acid present, the barium salt of which had been removed in the mother-liquors, and resorted to fractional acidification with sulphuric acid to settle this point. For this purpose a quantity of the acid distillate, after treatment with ether, was converted into the calcium salt and treated with one third of the amount of sulphuric acid necessary to set free all the acid it contained; it was then distilled with steam as long as the distillate showed an acid reaction. The residue in the flask was treated twice successively with the same amounts of sulphuric acid, and the first and third fractional distillates converted into calcium salts.

I. 0.3582 gr. of salt from the first fraction gave 0.2894 gr. of calcic sulphate.

II. 0.2281 gr. of salt from the third fraction gave 0.1980 gr. of calcic sulphate,

	Calculated for $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$.	I.	II.	Calculated for $\text{Ca}(\text{C}_3\text{H}_5\text{O}_2)_2$.
Calcium	25.32	23.76	25.54	21.50

From these numbers it appears that there is no large amount of any acid except acetic present, and the blackening and different crystalline forms of the silver salt were probably due to a trace of turmeric acid which could not be removed by ether.

As it was possible that a neutral lactone might have been formed, a portion of the acid liquid was boiled with baric carbonate, distilled with steam, and the neutral distillate boiled with baric hydrate for some time; as after removing the baric hydrate with carbonic dioxide there was no residue on evaporation no lactone was formed.

The formation of carbonic dioxide was determined by a special experiment, in which a portion of turmerol was oxidized out of contact with the air; upon acidifying with sulphuric acid a gas was given off, which gave a copious white precipitate with lime-water.

A. Study of the Distillate obtained from the Ether Extract with Steam.

This consisted principally of water, with a few yellow or brown oil-drops floating in it. It was extracted with ether, and the extract, which had acid properties, boiled with water and calcic carbonate. The solution of a calcium salt thus obtained, when allowed to evaporate spontaneously, deposited spherical collections of white needles and a yellow viscous substance somewhat more soluble than the crystals.

The crystalline body proved to be the calcium salt of the new acid, which we have called turmeric acid, after it had been purified by repeated crystallization from water, which is tedious in the highest degree, as all the solutions and evaporations have to be carried on at ordinary temperatures; in fact, it took us more than a year and a half to prepare and purify the four or five grammes of this substance, which have served for the present research.

In regard to the nature of the viscous non-crystalline salt we cannot speak with certainty, as we were unable to obtain it free from calcic turmerate; but we are of the opinion that it is a salt of an isomeric acid, as an analysis of the salt, which had not been purified by crystallization, gave 8.12 per cent of calcium instead of 8.93 calculated for calcic turmerate, and the acid set free from the amorphous salt remained liquid even at -5° , while turmeric acid solidifies at ordinary temperatures.

The total yield of mixed calcium salts cannot be more than one or two per cent of the turmerol oxidized, and the proportion of amorphous salt in this product is comparatively small.

Turmeric Acid. $C_{11}H_{14}O_2$. The calcium salt prepared and purified as just described was treated with hydrochloric acid, and then extracted with ether. On evaporating off the ether, a yellowish oil was left, which crystallized on standing, and gave the following analytical results after being dried *in vacuo*:—

- I. 0.2198 gr. of substance gave 0.5954 gr. of carbonic dioxide and 0.1586 gr. of water.
- II. 0.1320 gr. gave 0.3584 gr. of carbonic dioxide and 0.0960 gr. of water.

	Calculated for $C_{11}H_{14}O_2$.	I.	Found. II.
Carbon	74.16	73.87	74.04
Hydrogen	7.86	8.02	8.08

Properties. The turmeric acid, as at first precipitated, is an oil, which gradually solidifies in long white branching needles, or crystalline masses with a faint smell like cocoanut; freed from oil by pressing between filter-paper it melts at 34° – 35° ; it is slightly soluble in water, very freely in all the other common solvents except methyl-alcohol, in which, however, it is readily soluble, so that it was found impossible to crystallize it from this or any other solvent; it distils slowly with steam, and is a monobasic acid. When oxidized with a hot solution of potassic permanganate, not in too great excess, it gives the apoturmeric acid, which will be described later in this paper.

Calcic Turmerate. $Ca(C_{11}H_{13}O_2)_2 \cdot 3H_2O$. The preparation and purification of this salt have been described in connection with the manufacture of turmeric acid. For analysis it was dried, at first *in vacuo*, and afterward at 100° or 110° , when several agreeing analyses gave the percentage of calcium 10.78–11.13, whereas calcic turmerate contains only 10.15 per cent of calcium. This led us to suspect that the salt had undergone a constant decomposition at this temperature, which we were the more inclined to do, because at first it lost weight very rapidly, but later the loss dropped to a few milligrammes a day, and more than a week of continuous heating was necessary to obtain a constant weight, while at the same time the salt gradually became brown and viscous. We have therefore calculated our results upon the salt dried *in vacuo*, and these agree very well with the amount of calcium in calcic turmerate containing three molecules of water of crystallization.

I. 0.3131 gr. of substance dried *in vacuo* gave 0.0970 gr. of calcic sulphate.

II. 0.2993 gr. gave 0.0912 gr. of calcic sulphate.

	Calculated for $Ca(C_{11}H_{13}O_2)_2 \cdot 3H_2O$.	I.	Found. II.
Calcium	8.93	9.11	8.96

Properties. It forms spherical collections of white radiating needles looking like chestnut-burs; the purer the salt the more distinct are the separate needles. When boiled with water it melts to a viscous mass, which is then acted on by the water only very slowly; it is therefore advisable to dissolve it in the cold.

7.861 gr. of the solution saturated at 16° gave 0.0344 gr. of calcic sulphate. Therefore a saturated solution at 16° contains 1.27 per cent of $Ca(C_{11}H_{13}O_2)_2$.

The salt is also soluble in alcohol, and is decomposed by a heat of 100° – 110° , as already stated.

The behavior of a solution of the calcium salt with various reagents was also studied, and it was found to give a white flocculent precipitate with aluminic chloride; a similar reddish-brown precipitate with ferric chloride; heavy white precipitates with mercurous or plumbic salts, the plumbic salt melting under boiling water and forming, when prepared in quantity, an uninviting yellowish viscous mass; cupric nitrate produced pale-blue flocks, and argentic nitrate a heavy white precipitate somewhat soluble in water; the other common reagents gave no characteristic precipitates.

An attempt was made to prepare and analyze the *silver salt*, but we did not succeed in purifying it, since its solubility in water is so great that the impurities could not be removed by washing without using a larger amount of substance than was at our disposal; and it was impossible to recrystallize it from water, as its solutions decomposed with great ease. An imperfectly washed specimen gave a result which approaches that required by theory.

0.1932 gr. of the salt dried *in vacuo* gave 0.0750 gr. of silver.

	Calculated for $\text{AgC}_{11}\text{H}_{18}\text{O}_2$.	Found.
Silver	37.89	38.82

The *barium salt* resembled the calcium salt in that it formed little balls of radiating needles, but showed a much greater tendency to separate in a viscous state, so that it was hard to obtain it crystallized.

The behavior of the *zinc salt* is very characteristic; when a solution of it is prepared by boiling the acid with water and zincic oxide, allowing the liquid to cool, and filtering, the clear solution thus obtained becomes turbid, when warmed even to temperatures far below the boiling-point, but clears up again as the liquid cools. The salt could be obtained only as a viscous mass.

B. *Study of the Residue from Distillation with Steam.*

The flask-residue, after the turmeric acid had been distilled off with steam, contained a black tarry substance, and not infrequently a white crystalline acid, which can be separated from the tar by treatment with boiling water. On extracting with ether the aqueous mother-liquor, from which the white acid had crystallized, a third substance, yellow and buttery, was obtained. All these substances are acids,

but we have been unable to bring the black tarry acid or the yellow buttery one into a state fit for analysis, and can only say that the very ill-defined calcium salt of the former contained 1.69 per cent of calcium, while the latter gave on oxidation an acid melting near 180° , which was not phthalic acid, and was formed in such small quantity that we were unable to determine whether it was a pure substance or only a mixture of apoturmeric acid with some impurity.

Apoturmeric Acid. The white crystalline acid was separated from its impurities by crystallization from boiling water, till it showed a constant melting-point. The same acid is obtained by oxidizing calcic turmerate with a hot solution of potassic permanganate, and a good part of the substance used for analysis was prepared in this way; the yield, however, was so small, not over 10 per cent of the turmeric acid used, that we have been unable to determine even its formula with certainty, as will be seen from the following analyses.

0.1138 gr. of substance gave 0.2582 gr. of carbonic dioxide and 0.0590 gr. of water.

	Calculated for $C_{10}H_{10}O_4$.	Found.	Calculated for $C_{10}H_{12}O_4$.
Carbon	61.86	61.87	61.22
Hydrogen	5.15	5.76	6.12

The *calcium salt* made by boiling the acid with calcic carbonate and water gave the following results:—

I. 0.2274 gr. of salt dried *in vacuo* lost 0.0304 gr. when heated to 100° .

II. 0.1390 gr. lost 0.0186 gr. when heated to 100° .

	Calculated for $CaC_{10}H_8O_4 \cdot 2H_2O$.	Found.		Calculated for $CaC_{10}H_{10}O_4 \cdot 2H_2O$.
		I.	II.	
Water	13.43	13.36	13.39	13.33

0.1826 gr. gave 0.3370 gr. of carbonic dioxide, 0.0758 gr. of water, and 0.1016 gr. of calcic sulphate.

	Calculated for $CaC_{10}H_8O_4$.	Found.	Calculated for $CaC_{10}H_{10}O_4$.
Carbon	51.72	50.32	51.29
Hydrogen	3.40	4.61	4.27
Calcium	17.24	16.36	17.10

The *barium salt* prepared like the calcium salt gave a result which is not in harmony with the preceding.

0.2704 gr. of salt dried at 100° gave 0.1742 gr. of baric sulphate.

	Calculated for $BaC_{10}H_8O_4$.	Found.	Calculated for $BaC_{10}H_{10}O_4$.
Barium	41.64	37.87	41.39

If, however, we suppose that the salt retained two molecules of water at 100° , the result agrees very well with the calculated per cents.

	Calculated for $\text{BaC}_{10}\text{H}_8\text{O}_4\cdot 2\text{H}_2\text{O}$.	Found.	Calculated for $\text{BaC}_{10}\text{H}_{10}\text{O}_4\cdot 2\text{H}_2\text{O}$.
Barium	37.53	37.87	37.32

But this supposition is, to say the least, improbable, as the calcium salt loses its water easily at 100° ; unfortunately, we did not have enough of the acid to repeat the analysis of the barium salt.

Properties. The apoturmeric acid separates from its solution in boiling water as a white, rather stiff, wooly mass, which renders the whole solid, if the solution was a strong one; it melts at 221° , and is easily soluble in alcohol, ether, and boiling water; nearly insoluble in cold water.

Ammonic apoturmerate is not very freely soluble, and gives the following characteristic precipitates: With plumbic acetate, white flocculent; with cupric sulphate, whitish green, — both soluble in an excess of the precipitant; with mercurous nitrate, white flocks; with ferric chloride, yellowish white; with argentic nitrate, a heavy white precipitate, slightly soluble in boiling water. With the other common reagents it gives no precipitates at all, or very slight white ones.

Several attempts were made to oxidize the apoturmeric acid, but they gave no satisfactory result. The acid was attacked only with difficulty either by potassic permanganate or chromic anhydride, and the only insoluble substance left after the oxidation was simply undecomposed apoturmeric acid. In no case have we observed the formation of terephthalic acid from apoturmeric, or from carefully purified turmeric acid; but this acid has appeared when a calcic turmerate containing the non-crystalline impurity was oxidized. We should therefore ascribe the formation of terephthalic acid from turmerol by violent oxidation rather to this substance than to the turmeric acid formed; but our experiments must be repeated on a larger scale before we can consider this point finally settled.

It is to be regretted that we were unable to settle definitely the composition of the apoturmeric acid, as this would have thrown much light on the constitution of turmeric acid; as it is, it is not worth while to advance any hypotheses on this subject.

We may add one more observation in reference to turmerol, viz. isobutylturmerol does not give an addition-product with bromine, but there is formed with evolution of hydrobromic acid a most uninviting unstable viscous oil.